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Energetic Ionic Liquids Based on Anionic Rare Earth Nitrate Complexes (PREPRINT)

Guo-Hong Tao,^[a] Yangen Huang,^[a] Jerry A. Boatz,^[b] and Jean'ne M. Shreeve*^[a]

Abstract: Energetic ionic liquids based on anionic rare earth nitrate complexes, $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$, where Cat^+ is guanidinium, 4-amino-triazolium, 1-methyl-4-amino-triazolium, 1-ethyl-4-aminotriazolium, 1-butyl-4-amino-triazolium, 1,5-diamino-tetrazolium, and 1,5-diamino-4-methyltetrazolium, were prepared. The hexanitrate lanthanum (cerium) salts with the latter

two cations are the first CO-balanced energetic ionic liquids that are hydrolytically and air stable with impact sensitivities of ~ 27 J. For environmental considerations, these ionic liquids were obtained by a simple method using nitrate-containing precursors. All salts are fully characterized by IR, NMR, elemental analysis, thermal stability, phase

behavior, density, and water content determinations. Based on theoretical calculations, these new compounds have potential as propellants.

Keywords: CO-balanced · energetic ionic liquids · hydrolytically and air stable · rare-earth nitrate complexes · theoretical calculations

Introduction

Ionic liquids are often considered as greener solvents, electrolytes, and advanced materials.^[1] Compared with traditional energetic compounds, such as TNT, HMX, and RDX, many energetic ionic liquids were reported with several advantages, including enhanced thermal stability, higher densities, negligible vapor pressure, and little or no vapor toxicity.^[2] In 2006, the first CO-balanced energetic ionic liquid, 1-ethyl-4,5-dimethyltetrazolium tetranitratealuminate, was reported.^[3] The latter shows a glass transition temperature (T_g) at -46 °C. However, it is only stable in dry air, and thus must be protected from water. At 75 °C, clear weight loss which is attributed to the loss of NO_2 and oxygen and accompanied by the formation of Al-O-Al bridges was observed. Its initial preparation involved highly toxic and corrosive chemicals, N_2O_4 and NOCl .

Ligands which coordinate *via* oxygen atoms to a rare earth metal ion give rise to stable complexes. Thus higher air and thermal stabilities may be obtained by introducing rare earth metal nitrates

as main components of ionic liquids. We now report new energetic ionic liquids based on anionic rare-earth nitrate complexes, $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$. Based on CO formation, some of these salts have a neutral or positive oxygen balance. Compounds **11** and **12** are the first CO-balanced energetic ionic liquids which are stable to moisture and air. Furthermore, important for ease of synthesis and for environmental reasons, these liquids are prepared by using readily available nitrate salts as precursors.

Lanthanide-doped ionic liquids exhibit interesting luminescent properties and good photochemical stability.^[4] In addition to our present work, only one or two families of rare-earth metal ionic liquids have been prepared^[5], e. g., as inorganic polyoxometalate salts, $\text{Na}_{13}[\text{Ln}(\text{TiW}_{11}\text{O}_{39})_2] \cdot x\text{H}_2\text{O}$ (x varies between 27 and 44)^[5a] or where the lanthanides are coordinated with the pseudohalide, SCN^- , resulting in the hydrolytically unstable $[\text{bmim}]\text{Ln}(\text{SCN})_7$.^[5b] However, the former exist as hydrates and are not stable in the absence of water of hydration and are not typical ionic liquids. The instability of $[\text{bmim}]\text{Ln}(\text{SCN})_7$ to moisture and air also limits their applications. Since our new rare-earth ionic liquids do not present these difficulties, their potential for applications related to electrodeposition, catalysis, energetics or photophysics may be realized.

Results and Discussion

The nitrate is a familiar stable ligand for rare earth metals.^[6] It is an energetic oxidizing anion and may be the oxidizer component in energetic ionic liquids.^[7] Rare earth metals coordinate with *O*-donor ligands more strongly than *N*-donor ligands,^[8] e. g., in $[\text{bmim}]\text{Ln}(\text{SCN})_7$ ionic liquids, ambient moisture will displace the isothiocyanate ligand irreversibly decomposing the ionic liquid.^[5b] In our syntheses, as an example, guanidinium nitrate and lanthanum or cerium nitrate are dissolved in acetonitrile and refluxed with

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trimethyl orthoformate to give **1** or **2**. They are unchanged after being dissolved in water and dried in vacuum. Compounds **1** and **2** may be crystallized from water at room temperature to form colorless block-like crystals ($(\text{CH}_6\text{N}_3)_2[\text{La}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$, (**1**) and $(\text{CH}_6\text{N}_3)_2[\text{Ce}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ (**2**). The crystal structure of **1** was reported earlier.^[9]

Because of strong hydrogen bond interactions, the melting points of **1** and **2** exceed 100 °C. In order to reduce the melting points, substituted 1-amino-1,2,4-triazolium cations were introduced resulting in the formation of salts **5**–**10** using a minor modification of the literature method (Scheme 1).^[10] Stoichiometric amounts of triazolium iodide, AgNO_3 and lanthanum nitrate hexahydrate were refluxed in acetonitrile in the absence of light. After the silver iodide and the solvent were removed, a viscous liquid remained. These salts have the characteristics of room temperature ionic liquids. It was also our aim to increase the energy of these ionic liquids by selecting an energetic cation, such as the 1,5-diamino-4*H*-1,2,3,4-tetrazolium cation and 1,5-diamino-4-methyl-1,2,3,4-tetrazolium cation. The melting points of the salts, **11** and **12**, which contain the latter cation are lower than 100 °C which places the salts in the ionic liquid class. This preparative method for metal nitrate complexes is a relatively green procedure not involving highly toxic or corrosive chemicals.

In the IR spectra of salts **5** and **8**, (Figure 1), the main N-O stretching modes of the rare-earth anions, $[\text{Ln}(\text{NO}_3)_6]^{3-}$, are observed at about 1450–1470 cm^{-1} , 1320–1350 cm^{-1} , 1034–1040 cm^{-1} , 815–820 cm^{-1} in each of the energetic ionic liquids. These bands are assigned to the N-O stretching modes ν_4 , ν_1 , ν_2 , and bending mode ν_6 . Bands, ν_4 and ν_1 , are assigned to the N-O asymmetrical stretching vibration. Band ν_2 is composed of the N-O symmetrical stretching vibration and ν_6 is the out-of-plane bending vibration.^[11] These bands are characteristic of chelating bidentate nitrate ligands.^[12] Generally, the $\nu_3(E')$ of D_{3h} point group in the symmetric nitrate ion gives an IR absorbance band around 1385 cm^{-1} .^[11] When the oxygen atoms of the nitrate group coordinate with a rare earth metal, the N-O asymmetrical stretching vibration is perturbed and has two different stretching modes. Therefore, in the system with bidentate nitrate ligands, ν_3 is split into two peaks, ν_4 and ν_1 . In the $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ ionic liquids, the band separation ν_4 – ν_1 approaches 130 cm^{-1} . This distinguishes them from general nitrate ionic liquids which have no coordination structure.¹³ Furthermore, no other N-O stretching mode was found. It shows that all six of the nitrate ligands coordinated to each of the rare earth metals are bidentate.

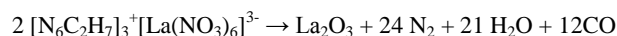
The salts, $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$, are thermally stable over the range of 185 to 235 °C in ambient nitrogen. In these new salts, the different cations play a more important role than the anion in determining the decomposition temperatures because they are less stable than the anions. As a whole, they are generally sufficiently thermally stable to meet the criterion for energetic compounds. It can be seen from Table 1 that all of the $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ salts, **3** to **12**, are ionic liquids. The melting points/glass transition temperatures (T_m/T_g) were determined by differential scanning calorimetry (DSC) from the first heating cycle. As the temperature is increased, the solid samples exhibit distinct melting points (T_m). The DSC curves of some solid samples, **1** (T_m 137 °C), **4** (T_m 76 °C), and **12** (T_m 90 °C), are given in Figure 2. However, on warming from -70 °C, liquid samples, **5** – **10**, behave differently. Each of them displays a gradual step associated with a phase transition temperature, T_g , between -20 to -40 °C. Since there is no sharp

endothermic peak that can be associated with melting as was observed in the liquid samples, **5** was taken as representative and examined further. When **5** was cooled to -70 °C, it became a glassy, transparent solid. After being warmed to > -25 °C, it gradually became a very viscous transparent liquid. This indicates that below their glass transition temperatures, they exhibit a glass-like character similar to that of conventional ionic liquids.^[14] Furthermore, different cations clearly affect the T_m and T_g . When the substituent on the 1-amino-1,2,4-triazolium cation was H or CH_3 , the product **3** or **5** has a very different phase transition point; however, as expected the difference in this property among alkyl substituent groups (CH_3 , C_2H_5 and C_4H_9) is trivial. This phenomenon arises from the greater opportunity for hydrogen bonding in the case of **3**. Although **3**, **4**, **11**, and **12** are solids, they readily form long-lived supercooled phases and solidify only after standing at room temperature for several days.

The densities of these rare earth ionic liquids vary from ~ 1.6 to 2.1 g/cm^3 with **11** and **12** being the most dense at 2.1 g/cm^3 . The 1,5-diamino-4-methyl-1,2,3,4-tetrazolium cation has a major impact on enhancing the density. In these $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ ionic liquids, the ratio of cation to anion is 3:1. In this case, the nitrogen content in each molecule will be improved since the majority of the nitrogen atoms are present in the cation. The calculated nitrogen content for the CO-balanced aluminum-containing ionic liquid is 28 %, ^[3] while the nitrogen content of CO-balanced salts **11** and **12** is ~40 %. This will advance the energetic performance of our new compounds.

These ionic liquids are hydrophilic and are soluble in water and low alcohols. Their water content was determined by using a Karl-Fischer coulometer. The water content, determined after the ionic liquid was dried under vacuum, ranges between 1900–4500 ppm. This is slightly higher than that found in conventional ionic liquids.^[13, 15] However, water does not affect the structure of these salts. In aqueous solution, the IR spectra show the absorbance peak at 1385 cm^{-1} which is assignable to the nitrate anion. After the liquids were dried, the infrared spectral absorbance peaks of the bidentate nitrate ligands near 1450 cm^{-1} and 1325 cm^{-1} reappeared concomitantly. At the same time, the peak at 1385 cm^{-1} disappeared. This is a reversible process and indicates that these materials are moisture stable ionic liquids.

Oxygen balance shows the deficiency or excess of oxygen in an energetic compound. In order to be a CO-balanced ionic liquid, the oxygen present must convert all of the C to CO, all of the H to H_2O , and all of the rare earth metal to Ln_2O_3 . The $\text{OB}_{\text{CO}}(\%)$ data of these ionic liquids are shown in Table 1. The OB_{CO} of **11** and **12** are zero, which indicates they are CO-balanced ionic liquids. When 1 mg **11** was heated to 200 °C in a micro melting point apparatus, gases rapidly evolved to leave white lanthanum oxide powder. The decomposition process is in accord with the predicted idealized combustion process.



The theoretical performance of $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ as propellants can be estimated from data calculated by the GAMESS^[16] and Gaussian 03 (Revision D.01) suites of programs. The heats of formation of the anions ($\Delta H_f^\circ(\text{anion})$) were estimated based on the gas-phase experimental heats of formation of NO_3^- , F^- , Cl^- , LaF_4^- and LaCl_4^- . Geometry optimizations and single-point calculations of the lanthanum-containing anions were performed using second-

order many body perturbation theory (MBPT(2),^[17] also known as MP2) in conjunction with the averaged relativistic effective core potentials (AREP) and the corresponding uncontracted valence-only basis sets.^[18, 19] For the cerium-containing anions, the Stevens, Basch, Krauss, Jaisan, and Cundari (SBKJC) effective core potentials and corresponding valence-only basis sets^[20] were used. The AREP and SBKJC basis sets for carbon, nitrogen, oxygen, fluorine, and chlorine were augmented with a diffuse s+p shell^[21] and a d-type polarization function.^[22] The heat of formation of the cations [$\Delta H_f^\circ(\text{cation})$] was determined by using the method of isodesmic reactions (**Figure 3**).^[23] The geometric optimization and the frequency analyses are carried out at the level of Becke three Lee-Yan-Parr (B3LYP) parameters up to 6-31+G(d,p) basis sets.^[24] Single energy points were calculated at the MP2/6-311++G(d,p) level.^[17a, b] Estimated heats of formation are obtained based on Born-Haber energy cycles (Equation I).^[23] The lattice energy (ΔH_L) is predicted by the formula suggested by Jenkins et al. (Equations II and III).^[25]

$$\Delta H_f^\circ(\text{ionic salts, 298K}) = \sum \Delta H_f^\circ(\text{cation, 298K}) + \sum \Delta H_f^\circ(\text{anion, 298K}) - \Delta H_L \quad (\text{I})$$

$$\Delta H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (\text{II})$$

$$U_{\text{POT}}/\text{kJ mol}^{-1} = 2342.6 * I^*(\rho_m/M_m)^{1/3} + 55.2 * I \quad (\text{III})$$

The heats of formation for $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ were calculated and are summarized in **Table 1**. Compound **14** has the highest value. The data show the performance of $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ may be better than some important energetic materials, such as hydrazine.^[3]

The impact sensitivity of **11** and **12** were measured by using a BAM method.^[26] The impact sensitivities of **11** and **12** are both 27 J (3/6 explosions and 2/6 explosions). This shows they are impact sensitive energetic materials.^[27]

Conclusions

The anionic rare earth nitrate complexes were found to be suitable anions to prepare energetic ionic liquids. The ionic liquids, $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$, are obtained by an environmental benign

preparative method using nitrate salts. Compounds **11** and **12** are the first CO-balanced metal ionic liquids which are stable to moisture and in air. Based on theoretical calculations, these liquids are potential propellants. Their thermal stabilities, phase behavior, densities, and water content have been investigated. Salts, $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$, may retain rare-earth metals in a stable liquid, thus possessing potential for applications related to electrodeposition, catalysis, or photophysics.

Experimental Section

Caution: We have not experienced any problems in handling these compounds. With the exception of **11** and **12**, their shock and impact sensitivities have not been determined. Therefore, they should be synthesized in less than one mmol amounts and handled with extreme care.

General Methods. All chemicals were pure analytical grade materials obtained commercially and used as received. IR spectra were recorded using KBr plates for neat liquids and KBr pellets for solids using a Biorad model 3000 FTS spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer operating at 300 and 75 MHz, respectively, by using CD₃CN, D₂O or *d*-₆-DMSO as a locking solvent. Chemical shifts are reported in ppm relative to TMS. The densities of the solid salts were measured at 25 °C using a Micromeritics Accupyc 1330 gas pycnometer. Differential scanning calorimetry (DSC) measurements were performed using a calorimeter equipped with an autocool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooling from 40 °C to -80 °C and heating to 400 °C at 10 °C/min. Thermogravimetric analysis (TGA) measurements were carried out by heating samples at 10 °C/min from 25 to 500 °C in a dynamic nitrogen atmosphere (flow rate 70 mL/min). Elemental analyses (H, C, N) were performed on a CE-440 Elemental Analyzer. The metal content was determined by EDTA titration. The water content was determined by coulometric Karl-Fischer titration using a Mettler Toledo DL39 Coulometer with a Hydranal® Coulomat AG reagent. Computations were performed by using the Gaussian 03 (Revision D.01) suite of programs.^[28]

Triguanidinium hexanitratolanthanum, 1. Guanidinium nitrate (3 mmol, 366 mg) and lanthanum nitrate hexahydrate (1 mmol, 433 mg) were refluxed in acetonitrile for 12 h. An excess of triethyl orthoformate was added during reflux to remove coordinated water. After being concentrated in vacuo, the resulting crude solid was washed from acetonitrile/ethyl ether. A quantitative yield of **1** as a white solid was obtained after drying under vacuum (692 mg). IR (KBr): 3493, 3417, 3383, 3214, 1695, 1660, 1581, 1472, 1420, 1355, 1323, 1294, 1034, 816, 743, 525 cm⁻¹; ¹³C NMR (D₂O): 167.1; Anal. Calcd for C₃H₁₈LaN₁₅O₁₈ (MW 691.17): C, 5.21; H, 2.62; N, 30.40; La 20.10; Found: C, 5.80; H, 2.86; N, 30.01; La, 20.11.

Triguanidinium hexanitrocercium, 2. The same procedure was used as for **1**. Guanidinium nitrate (3 mmol, 366 mg) and cerium nitrate hexahydrate (1 mmol, 434 mg) were used to obtain a quantitative yield of **2** as a white solid (692 mg). IR (KBr):

Table 1. Properties of $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$

Ionic liquid	T_m (T_g) ^a (°C)	T_d ^b (°C)	d^c (g/cm ³)	OB _{CO} ^d (%)	ΔH_f^e (cation) (kJ/mol)	ΔH_f^f (anion) (kJ/mol)	ΔH_L^g (kJ/mol)	ΔH_f^h (kJ/mol)	ΔH_f^i (kJ/g)
1	137	225	1.95	10.4	575.9	-1924.5	2327.2	-2524.0	-3.65
2	138	220	1.96	10.4	575.9	-1911.6	2329.4	-2513.3	-3.63
3	81	211	1.87	6.3	910.7	-1924.5	2233.5	-1425.9	-1.86
4	76	212	1.88	6.3	910.7	-1911.6	2235.9	-1415.4	-1.84
5	(-24)	231	1.76	-5.9	866.6	-1924.5	2162.9	-1487.6	-1.84
6	(-28)	227	1.77	-5.9	866.6	-1911.6	2165.4	-1477.2	-1.82
7	(-32)	232	1.67	-16.9	828.2	-1924.5	2101.3	-1541.2	-1.81
8	(-33)	228	1.67	-16.9	828.2	-1911.6	2100.4	-1527.4	-1.79
9	(-33)	229	1.59	-36.0	782.6	-1924.5	2019.1	-1595.8	-1.71
10	(-37)	230	1.60	-35.9	782.6	-1911.6	2021.9	-1585.7	-1.69
11	88	185	2.06	0	974.3	-1924.5	2224.4	-1226.0	-1.43
12	90	187	2.08	0	974.3	-1911.6	2229.6	-1218.3	-1.42
13	-	187	2.00	11.79	1018.0	-1924.5	2237.6	-1108.1	-1.36
14	-	188	2.02	11.77	1018.0	-1911.6	2242.9	-1100.5	-1.35
OB-EIL3ⁱ			0		836	-1486	419	-1069	-2.66

^a Melting point/phase transition temperature. ^b Thermal degradation. ^c Density, gas pycnometer, 25 °C. ^d CO oxygen balance OB_{CO}(%)—index of the deficiency or excess of oxygen in a compound required to convert all C into CO, all H into H₂O and all rare earth metals to metal oxides. For a compound with the molecular formula of C_aH_bN_cO_dM_e, OB_{CO}(%) = 1600[(*d* - *a* - *b*/2 - 3*e*/2)/MW] (M, rare earth metal; MW, molecular weight of salt). ^e Molar enthalpy of the formation of cation. ^f Molar enthalpy of the formation of anion. ^g Lattice energy. ^h Molar enthalpy of the formation of salt. ⁱ Reference 3

3493, 3416, 3380, 3214, 1693, 1660, 1580, 1472, 1418, 1358, 1325, 1296, 1035, 815, 743, 522 cm⁻¹; ¹³C NMR (D₂O): 166.9; Anal. Calcd for C₃H₁₈CeN₁₅O₁₈ (MW 692.38): C, 5.20; H, 2.62; N, 30.34; Ce 20.24; Found: C, 5.39; H, 3.01; N, 30.24; Ce, 20.13.

Tri(4-amino-1H-1,2,4-triazolium) hexanitratolanthanum, 3. The same procedure was used as for **1**. 4-Amino-1H-1,2,4-triazolium nitrate (3 mmol, 441 mg) and lanthanum nitrate hexahydrate (1 mmol, 433 mg) were used to obtain a quantitative yield of **3** as a colorless viscous transparent liquid (760 mg) which became a light yellow solid after standing at 25 °C for one week. IR (KBr): 3397, 3144, 1635, 1458, 1341, 1075, 1038, 939, 879, 825, 738, 617 cm⁻¹; ¹H NMR (CD₃CN): 8.97 (s, 2H), 3.84 (br, 2H); ¹³C NMR (CD₃CN): 145.1; Anal. Calcd for C₆H₁₅LaN₁₈O₁₈ (MW 766.20): C, 9.41; H, 1.97; N, 32.91; La 18.13; Found: C, 9.53; H, 2.06; N, 33.66; La, 17.91.

Tri(4-amino-1H-1,2,4-triazolium) hexanitratocerium, 4. The same procedure was used as for **1**. 4-Amino-1H-1,2,4-triazolium nitrate (3 mmol, 441 mg) and cerium nitrate hexahydrate (1 mmol, 434 mg) were used to obtain a quantitative yield of **4** as a colorless viscous transparent liquid (764 mg) which became a light yellow solid after one week at 25 °C. IR (KBr): 3200, 3136, 1636, 1456, 1323, 1075, 1039, 934, 878, 816, 738, 621 cm⁻¹; ¹H NMR (CD₃CN): 8.98 (s, 2H), 3.20 (br, 2H); ¹³C NMR (CD₃CN): 145.2; Anal. Calcd for C₆H₁₅CeN₁₈O₁₈ (MW 767.41): C, 9.39; H, 1.97; N, 32.85; Ce 18.26; Found: C, 9.57; H, 1.96; N, 32.67; Ce, 18.13.

Tri(4-amino-1-methyl-1,2,4-triazolium) hexanitratolanthanum, 5. The basic technique used follows closely that employed in the literature in preparing the tetrabutyl ammonium hexanitrate complexes.^[10] 4-Amino-1-methyl-1,2,4-triazolium iodide was obtained *via* a minor modification procedure of literature methods.^[29] A mixture of 4-amino-1,2,4-triazole (2 mmol, 168 mg) and iodomethane (2 mmol, 284 mg) in acetonitrile (20 mL) was stirred at room temperature for 5 d. The solution was concentrated and added to excess ethyl acetate (3-5 x volume of solution). After decanting the solvent, the residual solvent was removed from the lower layer in vacuo, to obtain a white solid (442 mg, 98%). IR (KBr) 3484, 3223, 3119, 1609, 1567, 1443, 1405, 1170, 1067, 973, 867, 730, 610 cm⁻¹. ¹H NMR (CD₃CN): 9.54 (s, 1H), 8.66 (s, 1H), 6.15 (s, 2H), 4.06 (s, 3H). ¹³C NMR (CD₃CN): 145.9, 143.9, 40.1. 1-Methyl-4-amino-1,2,4-triazolium iodide (0.3 mmol, 68 mg), AgNO₃ (0.3 mmol, 51 mg) and lanthanum nitrate hexahydrate (0.1 mmol, 43 mg) were held at reflux in acetonitrile for 12 h with complete exclusion of light. An excess of triethyl orthoformate was added during reflux to remove coordinated water. After the silver iodide was filtered off, the filtrate was concentrated. The resulting crude liquid was purified by dissolving in methanol (~10 mL), filtered, and the filtrate was added to ethyl ether (3-5 x volume of filtrate). The mixture was shaken, allowed to separate, and the top layer was decanted off. The process is repeated as necessary to ensure removal of the traces of silver iodide. Light yellow viscous liquid **5** was obtained after being dried under vacuum. Yield: 36 mg (45%). IR (KBr): 3332, 3241, 3148, 1632, 1574, 1454, 1325, 1172, 1072, 1038, 981, 877, 819, 735, 615 cm⁻¹; ¹H NMR (CD₃CN): 9.43 (s, 1H), 8.58 (s, 1H), 6.13 (br, 2H), 4.07 (s, 3H); ¹³C NMR (CD₃CN): 145.9, 144.0, 40.0; Anal. Calcd for C₉H₂₁LaN₁₈O₁₈ (MW 808.28): C, 13.37; H, 2.62; N, 31.19; La, 17.19; Found: C, 13.42; H, 2.63; N, 31.27; La, 17.19.

Tri(4-amino-1-methyl-1,2,4-triazolium) hexanitratocerium, 6. The same procedure was used as for **5**. 4-Amino-1-methyl-1,2,4-triazolium iodide (0.3 mmol, 68 mg), AgNO₃ (0.3 mmol, 51 mg) and cerium nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain a light yellow viscous liquid **6**. Yield: 39 mg (48%). IR (KBr): 3338, 3238, 3148, 1634, 1574, 1456, 1323, 1172, 1073, 1038, 981, 878, 818, 736, 616 cm⁻¹; ¹H NMR (CD₃CN): 9.62 (s, 1H), 8.71 (s, 1H), 6.30 (br, 2H), 4.20 (s, 3H); ¹³C NMR (CD₃CN): 146.0, 144.2, 40.2; Anal. Calcd for C₉H₂₁CeN₁₈O₁₈ (MW 809.49): C, 13.35; H, 2.61; N, 31.05; Ce, 17.31; Found: C, 13.68; H, 2.56; N, 30.90; Ce, 17.25.

Tri(4-amino-1-ethyl-1,2,4-triazolium) hexanitratolanthanum, 7. The same procedure was used as for **5**. 4-Amino-1-ethyl-1,2,4-triazolium iodide was prepared *via* the method used for 4-amino-1-methyl-1,2,4-triazolium iodide. A mixture of 4-amino-1,2,4-triazole (2 mmol, 168 mg) and iodoethane (2 mmol, 312 mg) in acetonitrile (20 mL) was reacted at 50 °C for 1 d. The solution was concentrated and added to excess ethyl acetate (3-5 x volume of solution). After decanting the solvent, any residual solvent was removed from the lower layer in vacuo, to obtain a yellow liquid, **7** (462 mg, 96%). IR (KBr) 3455, 3233, 3121, 3051, 1621, 1560, 1449, 1406, 1165, 1074, 989, 964, 872, 722, 619 cm⁻¹. ¹H NMR (CD₃CN): 9.89 (s, 1H), 8.81 (s, 1H), 6.39 (s, 2H), 4.43 (t, 2H, *J* = 7.2 Hz), 1.53 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (CD₃CN): 146.1, 143.3, 49.2, 14.2. 4-Amino-1-ethyl-1,2,4-triazolium iodide (0.3 mmol, 72 mg), AgNO₃ (0.3 mmol, 51 mg) and lanthanum nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain colorless viscous liquid **7**. Yield: 47 mg (55%). IR (KBr): 3332, 3233, 3135, 1631, 1566, 1459, 1323, 1198, 1167, 1075, 1038, 990, 872, 819, 735, 621 cm⁻¹; ¹H NMR (CD₃CN): 9.46 (s, 1H), 8.61 (s, 1H), 4.40 (t, 2H, *J* = 7.2 Hz), 3.68 (br, 2H), 1.53 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (CD₃CN): 145.9, 143.2, 49.1, 13.9; Anal. Calcd for C₁₂H₂₇LaN₁₈O₁₈ (MW 850.36): C, 16.95; H, 3.20; N, 29.65; La, 16.33; Found: C, 17.01; H, 3.50; N, 29.68; La, 16.29.

Tri(4-amino-1-ethyl-1,2,4-triazolium) hexanitratocerium, 8. The same procedure was used as for **7**. 4-Amino-1-ethyl-1,2,4-triazolium iodide (0.3 mmol, 72 mg), AgNO₃

(0.3 mmol, 51 mg) and cerium nitrate hexahydrate (0.1 mmol, 43 mg) were reacted to obtain colorless viscous liquid **8**. Yield: 45 mg (53%). IR (KBr): 3335, 3239, 3139, 1634, 1567, 1470, 1313, 1209, 1165, 1076, 1038, 992, 878, 819, 737, 621 cm⁻¹; ¹H NMR (CD₃CN): 9.72 (s, 1H), 8.75 (s, 1H), 4.52 (t, 2H, *J* = 7.2 Hz), 2.73 (br, 2H), 1.61 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (CD₃CN): 145.3, 143.5, 49.3, 14.0; Anal. Calcd for C₁₂H₂₇CeN₁₈O₁₈ (MW 851.57): C, 16.93; H, 3.20; N, 29.61; Ce, 16.45; Found: C, 15.94; H, 3.32; N, 29.62; Ce, 16.32.

Tri(4-amino-1-butyl-1,2,4-triazolium) hexanitratolanthanum, 9. The same procedure was used as for **5**. 4-Amino-1-butyl-1,2,4-triazolium iodide was prepared according to the similar method as for 4-amino-1-methyl-1,2,4-triazolium iodide. A mixture of 4-amino-1,2,4-triazole (2 mmol, 168 mg) and iodobutane (2 mmol, 368 mg) in acetonitrile (20 mL) was stirred at 70 °C for 12 h. The solution was concentrated and added to excess ethyl acetate (3-5 x volume of solution). After decanting the solvent, any residual solvent was removed from the lower layer in vacuo, to obtain a yellow liquid (516 mg, 96%). IR (KBr) 3460, 3246, 3120, 2961, 2874, 1622, 1561, 1524, 1462, 1407, 1381, 1163, 1073, 988, 864, 755, 617 cm⁻¹. ¹H NMR (CD₃CN): 9.87 (s, 1H), 8.77 (s, 1H), 6.40 (s, 2H), 4.39 (t, 2H, *J* = 7.2 Hz), 1.86~1.97 (m, 2H), 1.34~1.42 (m, 2H), 0.95 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (CD₃CN): 146.1, 143.6, 53.4, 31.1, 19.8, 13.6. 4-Amino-1-butyl-1,2,4-triazolium iodide (0.3 mmol, 80 mg), AgNO₃ (0.3 mmol, 51 mg) and lanthanum nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain colorless viscous liquid **9**. Yield: 49 mg (52%). IR (KBr): 3333, 3220, 3131, 2965, 2877, 1643, 1562, 1450, 1322, 1142, 1073, 1034, 993, 871, 820, 734, 631 cm⁻¹; ¹H NMR (CD₃CN): 9.46 (s, 1H), 8.60 (s, 1H), 6.11 (br, 2H), 4.37 (t, 2H, *J* = 7.2 Hz), 1.86~1.92 (m, 2H), 1.35~1.42 (m, 2H), 0.97 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (CD₃CN): 146.0, 143.5, 53.4, 31.1, 19.8, 13.5; Anal. Calcd for C₁₈H₃₉LaN₁₈O₁₈ (MW 934.52): C, 23.13; H, 4.21; N, 26.98; La, 14.86; Found: C, 23.04; H, 3.97; N, 27.13; La, 14.71.

Tri(4-amino-1-butyl-1,2,4-triazolium) hexanitratocerium, 10. The same procedure was used as for **9**. 4-Amino-1-butyl-1,2,4-triazolium iodide (0.3mmol, 80 mg), AgNO₃ (0.3 mmol, 51 mg) and cerium nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain colorless viscous liquid **10**. Yield: 52 mg (56%). IR (KBr): 3332, 3231, 3137, 2964, 2876, 1635, 1565, 1450, 1321, 1165, 1076, 1037, 990, 877, 819, 735, 618 cm⁻¹; ¹H NMR (CD₃CN): 9.73 (s, 1H), 8.73 (s, 1H), 6.30 (br, 2H), 4.50 (t, 2H, *J* = 7.2 Hz), 1.96~2.05 (m, 2H), 1.38~1.50 (m, 2H), 1.00 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (CD₃CN): 146.1, 143.7, 53.5, 31.2, 19.8, 13.5; Anal. Calcd for C₁₈H₃₉CeN₁₈O₁₈ (MW 935.73): C, 23.10; H, 4.20; N, 26.94; Ce, 14.97; Found: C, 23.08; H, 4.34; N, 27.23; Ce, 14.59.

Tri(1,5-diamino-4-methyl-1,2,3,4-tetrazolium) hexanitratolanthanum, 11. The same procedure was used as for **5**. 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium iodide was obtained *via* a minor modification of the literature procedure.^[30] A mixture of 1,5-diamino-1,2,3,4-tetrazole (2 mmol, 0.200 mg) and an excess of iodomethane (10 mmol, 1.42 g) in acetonitrile (60 mL) was refluxed for 18 h. The solution was concentrated and added to excess ether (5 x volume of solution). The crude product was gotten by filtration. After washing by ether, any residual solvent was removed in vacuo, to obtain a white solid (430 mg, 89%). IR (KBr): 3240, 3090, 1700, 1609, 1571, 1390, 1115, 1025, 785, 605, 522 cm⁻¹. ¹H NMR (CD₃CN): 7.65 (s), 6.12 (s, 2H), 4.00 (s, 3H); ¹³C NMR: 152.6, 36.7. 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium iodide (0.3 mmol, 73 mg), AgNO₃ (0.3 mmol, 51 mg) and lanthanum nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain the colorless viscous liquid **11**, which became a white solid after standing for three days. Yield: 41 mg (48%). IR (KBr): 3335, 3233, 3055, 1700, 1616, 1451, 1352, 1118, 1037, 912, 818, 735, 581 cm⁻¹; ¹H NMR (CD₃CN): 7.61 (s), 6.02 (s, 2H), 3.89 (s, 3H); ¹³C NMR (CD₃CN): 149.0, 35.6; Anal. Calcd for C₆H₇LaN₂₄O₁₈ (MW 856.28): C, 8.42; H, 2.47; N, 39.26; La, 16.22; Found: C, 8.43; H, 2.52; N, 38.38; La, 16.11.

Tri(1,5-diamino-4-methyl-1,2,3,4-tetrazolium) hexanitratocerium, 12. The same procedure was used as for **11**. 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium iodide (0.3 mmol, 73 mg), AgNO₃ (0.3 mmol, 51 mg) and cerium nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain the colorless viscous liquid **12** which became a white solid after standing at 25 °C for one day. Yield: 43 mg (50%). IR (KBr): 3339, 3260, 3050, 1700, 1617, 1459, 1350, 1118, 1038, 909, 818, 736, 576 cm⁻¹; ¹H NMR (CD₃CN): 7.61 (s), 6.12 (s, 2H), 3.96 (s, 3H); ¹³C NMR (CD₃CN): 149.1, 35.7; Anal. Calcd for C₆H₇CeN₂₄O₁₈ (MW 857.49): C, 8.40; H, 2.47; N, 39.20; Ce, 16.34; Found: C, 8.36; H, 2.49; N, 38.72; Ce, 16.32.

Tri(1,5-diamino-4-*H*-1,2,3,4-tetrazolium) hexanitratolanthanum, 13. The same procedure was used as for **1**. 1,5-Diamino-4-*H*-1,2,3,4-tetrazolium nitrate was obtained based on the literature procedure.^[30] 1,5-Diamino-4-*H*-1,2,3,4-tetrazolium nitrate (0.15 mmol, 27 mg), and lanthanum nitrate hexahydrate (0.05 mmol, 22 mg) were used to obtain the white solid **13**. Yield: 47 mg (96%). IR (KBr): 3324, 3273, 3156, 1721, 1658, 1467, 1330, 1110, 1038, 1004, 932, 816, 742, 689, 627 cm⁻¹; ¹H NMR (*d*₆-DMSO): 4.83 (s); ¹³C NMR (*d*₆-DMSO): 155.2; Anal. Calcd for C₆H₇LaN₂₄O₁₈ (MW 856.28): C, 4.43; H, 1.86; N, 41.29; La, 17.06; Found: C, 4.77; H, 1.85; N, 41.09; La, 16.91.

Tri(1,5-diamino-4-*H*-1,2,3,4-tetrazolium) hexanitratocerium, 14. The same procedure was used as for **13**. 1,5-Diamino-4-*H*-1,2,3,4-tetrazolium nitrate (0.15 mmol, 27 mg), and lanthanum nitrate hexahydrate (0.05 mmol, 22 mg) were used to obtain the

white solid **14**. Yield: 48 mg (98%). IR (KBr): 3343, 3266, 1717, 1629, 1466, 1329, 1130, 1037, 998, 925, 817, 740, 690, 623 cm⁻¹; ¹H NMR (*d*₆-DMSO): 4.95 (s); ¹³C NMR (*d*₆-DMSO): 155.4; Anal. Calcd for C₆H₂₁CeN₂₄O₁₈ (MW 857.49): C, 4.42; H, 1.85; N, 41.23; Ce, 17.18; Found: C, 4.67; H, 1.84; N, 41.12; Ce, 17.12.

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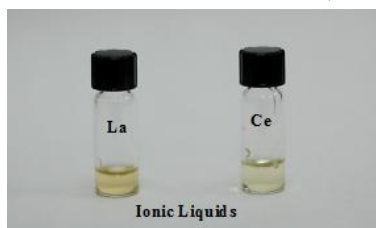
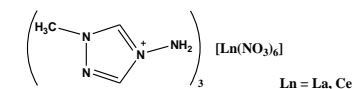
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Rare earth ionic liquids

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Energetic Ionic Liquids based on Anionic Rare Earth Nitrate Complexes



A novel series of energetic ionic liquids based on anionic rare earth nitrate complexes, $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$, were synthesized and characterized. Theoretical calculations show that the new salts may be considered to be potential propellants.

Scheme 1. Structures of ionic liquids based on anionic rare-earth nitrate complexes

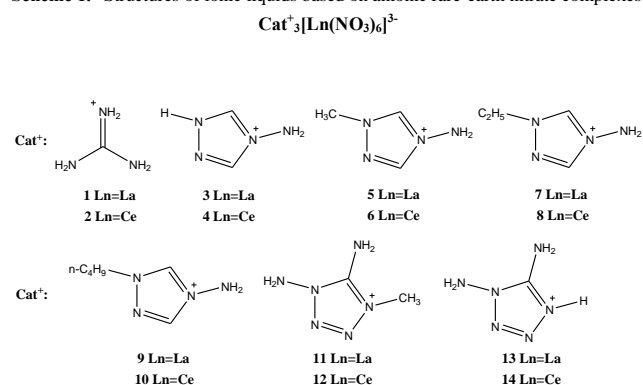


Figure 1. IR spectra of **5** and **8**. The stars mark the typical N-O vibration bands of the $[\text{Ln}(\text{NO}_3)_6]^{3-}$ anions.

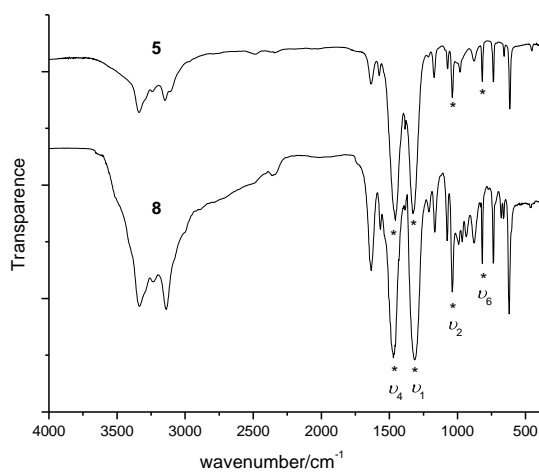


Figure 2. DSC curves of some typical ionic liquids, $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$.

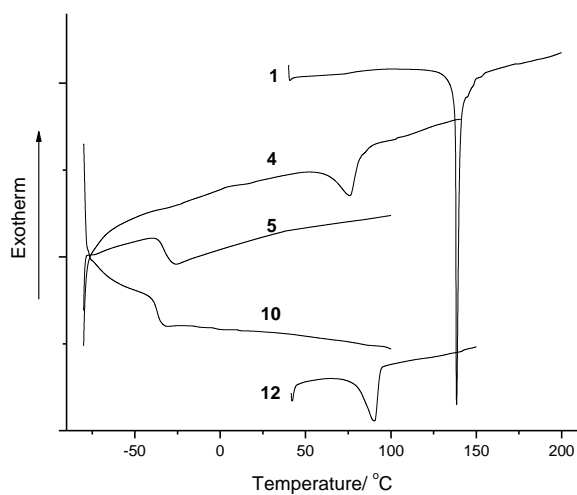


Figure 3. Isodesmic reactions and protonation reactions for the heats of formation of cations.

